Preparation, Properties and Dental Applications of Polycarboxylate cement

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By

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CERTIFICATE

This is to certify Mr. Tigmakar Tapan Kumar Brahma from Delhi college Of Engineering, Delhi has individually completed a Major project entitled "Preparation, Properties and Dental Applications of Polycarboxylate Cement" under the supervision of Dr. A.P. Gupta, H.O.D. Department of Polymer Technology and Applied Chemistry, Delhi College of Engineering, Delhi University, Delhi-110042 during the session 2001-2002 as fulfillment of Master of Engineering in Polymer Technology of Delhi University. This work has not been published anywhere for the award of any Degree.

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CONTENTS

CHAPTER 1
INTRODUCTION

Biomedical polymers have been used in a wide variety of applications including artificial limbs, bone cements, dental fillings, dentures, external ear repairs, surgical adhesives, sutures etc. Various materials have been used for these applications and no single material can fulfill all of these requirements.

The most modern and difficult area of application of biomedical polymers is in artificial organs. An artificial organ should be capable of implementation into the body and be able to replace totally the function of the disabled organ The basic requisite for usage of an artificial organ is the blood compatibility as many of them come into contact with blood. A number of polymeric systems have been explored to serve the purpose of blood compatibility.

Polymeric materials are rapidly entering into the field of dentistry. They are used in various dental applications such as denture base, artificial teeth, cavity restorations, resilient linings, crown and bridge materials, dental cements, root canal and impression materials.

Dental materials must meet the physical, chemical, biological and aesthetic requirements including adequate strength, resilience, abrasion resistance, dimensional stability in processing, translucency, colour stability, resistance to oral fluid, food or other substances with which the material may

come in contact. Polymers play an important role in operative dentistry as ingredients of composite restorative materials, cements and adhesives, cavity liners and protective sealants for pits and fissures.

1.1. BRIEF HISTORY OF DENTAL CEMENTS:

A general definition of cement is that it holds two surfaces together. However as far as "dentistry" is concerned, a cement serves as a cementing (luting) agent but also as an aesthetic restorative material and medicament for pulpal protection. Also it can be defined as a paste that hardens to a stony consistency applied soft for sticking things together.

In view of the varying demands in manipulative properties such as setting time, resistance to mechanical breakdown and dissolution in oral fluids, it is practically not possible to have a single type of material to perform satisfactorily under all conditions. Since 1920 cement based on Zinc Oxide and eugenol [the essential component (85%) of clove oil] has remained in use for almost 50 years. Subsequently several cements such as Zinc Phosphate, Silico-Phosphate, Polyalkenoate cement or Polyelectrolyte cements such as Polycarboxylate cement and glass-ionomer cements were developed.

Inorganic Cements:

Inorganic cements are two component systems, an inorganic powder and an acid. These are mainly Zinc Phosphate, Silicate, Silico-phosphate and Zinc Oxide eugenol cements.

2

a) Zinc Phosphate cement:

It is a two component system namely Zinc Oxide powder and an aqueous solution of orthophosphoric acid. The powder may contain small amounts of other oxides such as magnesium oxide as a modifier. Also Aluminium and Zinc are present as dissolved phosphates in the liquid.

$ZnO + H_3PO_4 \longrightarrow$ Amorphous Zinc Phosphate

b) Silicate Cement:

Silicate Cement is a two-component system consisting of Aluminosilicate glass as powder and the same orthophosphoric acid as in case of Zinc phosphate cement, but it contains a little more water here.

c) Silicophosphate Cement:

Silicophosphate Cement is a combination of Zinc phosphate and silicate cement. The powder is a blend of ZnO and silicate glass mixed or fused mechanically and subsequently powdered. The liquid is a concentrated orthophosphoric acid solution containing 45% water and 2.5% Aluminium and Zinc Phosphate salts.

d) Zinc Oxide-eugenol cement:

Here the powder is Zinc Oxide. The liquid is purified eugenol or in some cases eugenol (85% in clove oil). Acetic acid and water may be present to accelerate setting.

Although Zinc Oxide eugenol and the phosphate cements give an adequate performance in many clinical situations, their inadequate mechanical properties and liability to cause tissue irritation had led to an intensified search for new types of cements. During the period 1960-1970, the demand for properties, which would assure durability in the clinical environment, has been coupled with the necessity for adhesive properties to tooth substance. Thus much of the recent research in the dental field on the production of cementitious materials both for fillings and for cementing restorations into teeth, which would fulfill these objectives, has been directed towards the development of suitable polymer systems.

The stringent demands of the oral environment together with the operative techniques employed in clinical dentistry necessitate the use of biologically stable polymer materials. The epoxy resins and methyl methacrylate monomer-polymer systems are both areas in which interest and effort had been concentrated.

There are many clinical applications for dental cements. Medical uses of cements are fields of interest and have been confined primarily to prosthetic and reconstructive applications especially in orthopeadics and to the use of adhesive materials for the suture less closure and protection of wounds. The former application has benefited from dental research whereas the later, which was of equal interest in the dental field, has benefited from medical research. Thus there is a considerable common interest in materials, which can be moulded to replace lost tissue, which are biologically acceptable and adhesive

4

to soft or calcified (hardened due to the deposition of calcium carbonate or other calcium compounds) tissue.

Much effort has been devoted to the cyano-acrylates. Although they have received trial in many clinical, medical and dental applications, doubts appear to remain about their stability and toxicology. Epoxy and Polyurethane dental materials also have been tried which shows good adhesion to teeth and tissue.

A polymer–monomer (Polymethyl methacrylate and Methyl methacrylate) dough moulding technique had been exploited in 1938 for dentures which was heat cured. Towards 1950 considerable dental expertise in the manipulation of the polymer-monomer system led to cold curing materials used as denture base materials as well as fillings in teeth. The powder in such cements is essentially PMMA in the form of a mixture of the spherical and irregular particles containing 1% of benzoyl peroxide. The liquid is MMA (methyl methacrylate) monomer containing approximately 1% of N, N-Dimethyl para Toludine (as accelerator to the monomer) and less than 0.01% of polymerization inhibitor. The monomer and polymer are mixed in a ratio of 1:2 by weight when dissolution of a part of the polymer in the monomer and the polymerization of the monomer through the peroxide amine system occur. The dissolution process and rate of polymerization is controlled by the powder-liquid ratio. Polymerization of the monomer leads to a hard and rigid mass in about 6-10 minutes.

Several types of polymer systems such as epoxy resins and nylon have been tried as denture base materials and were shown to be unsatisfactory. Epoxy resins are dimensionally unstable and absorb water while nylon gets discoloured easily.

Acrylic resins have been the standard of usage since 1938 because of their colour and light stability, low water absorption and good dimensional stability when cured.

The PMMA-MMA system which has been used as dental filling material are less soluble and less brittle than silicate filling materials, but they suffer from a lack of adhesion and dimensional stability primarily due to their high co-efficient of thermal expansion relative to natural dentin or enamel. They also lack abrasion resistance, have a tendency to get discoloured because of the presence of the amine activator. Also they show pulp irritation and have some tendency to deform and flow under occlusal load.

Shrinkage during polymerization is another drawback in this system. Other monomers such as Trimethyl-cyclohexyl methacrylate and cyclohexyl methacrylate have shrinkages on polymerization of 10-12% as compared to 21% for MMA has also been tried. However these resins are considerably more brittle than the PMMA and still have high co-efficient of thermal expansion. It has been shown that acrylic resins when dry have an adhesive strength to enamel three times that of phosphate cement, but only one half the strength when wet.

Filling materials based on already formed resins such as Polystyrene, Nylon and Polycarbonates have been directly injected with hot syringe devices into the

6

cavity. Since this method generally requires the use of free flowing polymers, the addition of any filler is not practical. Also directly injecting the hot resin (150°C) into the cavity is a matter of concern.

1.2. POLYCARBOXYLATE CEMENTS:

Appreciable solubility and/or inadequate mechanical strength of the conventional materials result in a high incidence of failure. A material of improved durability, which also displays adhesion to the enamel and dentine of the tooth, must obviously be exceptional. The production of true adhesion to tooth substance is difficult because of factors affecting the production of a clean smooth surface. Besides the saliva itself, the external enamel is coated with an organic proteinaceous cuticle derived mainly from the saliva and the cut enamel and dentine surface (after the clinical preparation of a cavity in the tooth) will also be contaminated by saliva or dentine fluid, which exudes from the cut dentinal tubules.

Hence a clinically satisfactory adhesive material must be hydrophilic and should bond chemically to the enamel and dentine through strong polar attraction or specific interaction. Most such agents have been intended to react chemically with the calcium or phosphate groupings of the mineral phase of enamel or dentine or with the protein (which is largely collagen) in the dentine. Much effort has been devoted on the development of improved cements, which might show adhesion to calcified tissues. With respect to the function of dental

cement, however, the mineral phase is most accessible for chemical reaction. When the physiological conditions governing bonding to such an apatite (calcium phosphate) phase are considered, formation of a biologically stable chelate with calcium appears most satisfactory. Such chelates are formed by structures in which a carboxyl or carbonyl group is present together with a hydroxyl or amino group e.g. Citric acid, Tetracycline and Phenols of the eugenol type. Such structures are found also in materials, which naturally adhere to the teeth such as muco-proteins, dextrans (polysaccharides) and tobacco tars. A suitable material therefore would be a water-soluble polymer containing appropriate chelate groups. One such agent, which has been developed into usable cement, is Polyacrylic acid.

These polyacrylic cements are based upon an aqueous solution of polyacrylic acid. The material is therefore hydrophilic. The carboxyl groups are intended to chelate to calcium ions in the surface of the calcified tissue and to react in addition with other metal ions. They form complexes with proteins also. The actual cements known commercially as carboxylate or poly-carboxylate cements are produced by mixing the polyacrylic acid solution with modified (deactivated) Zinc Oxide powder.

Variation in the molecular weight and concentration of the polyacrylic acid in the solution permits the formulation of materials, which display a wide range of viscosity and setting time behaviour. This poly-carboxylate cement shows good strength and low tissue irritancy as well as greatly improved adhesion compared to conventional cements. The tissue reaction to these

materials has been assessed by customary methods including reaction of the dental pulp to trial fillings in dogs, monkeys and humans and by implementation in soft tissue and bone in rats and monkeys. The reactions of the pulpal tissues also showed a mild response even in cavities, which are very close to the pulp. The new bone has a normal appearance, which appeared slightly more favourable in the case of poly-carboxylate cement than the plaste· of paris controls. The implantation in soft tissues likewise showed little reaction as compared to the severe inflammation produced by conventional phosphoric acid cement materials.

1.3. SETTING CHEMISTRY:

The cement sets between the reactions of two main components (Zinc Oxide and Polyacrylic acid) to form a cross-linked structure of Zinc Polyacrylate. The set cement consists of residual ZnO and other particles bonded together by the amorphous gel like matrix

According to one of the theories proposed the hydrogen ions (protons) from polyacrylic acid penetrate into the powder particles liberating metal ions which migrate into the liquid (polyacrylic acid) where they combine with the anion to form a salt like gel matrix.

However hardening of the mix was attributed to the neutralization of the polyacrylic acid with the metal oxides and stiffening of the network by ionic

interactions of carboxylic groups with Zinc ions and reinforcing action of metal oxides is as shown in the following scheme.

40% Aq. Solution $\{$ CH$_2$-CH $\}_n$ + ZnO $\longrightarrow$
                |
               COOH

$\{$CH$_2$-CH – CH$_2$-CH – CH$_2$ – CH – CH$_2$-CH –CH$_2\}_n$-CH –COOH
     | | | |
    COOH   COOH   COOH   COOH
                        Zn^{2+}

    COOH   COOH   COOH   COOH
     | | | |
$\{$ CH$_2$-CH – CH$_2$-CH – CH$_2$ – CH – CH$_2$-CH –CH$_2\}_n$-CH –COOH

(Ref. 3)

Ca^{2+} Ca^{2+} Ca^{2+}
Enamel
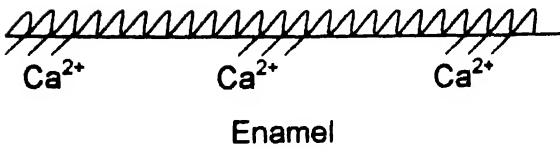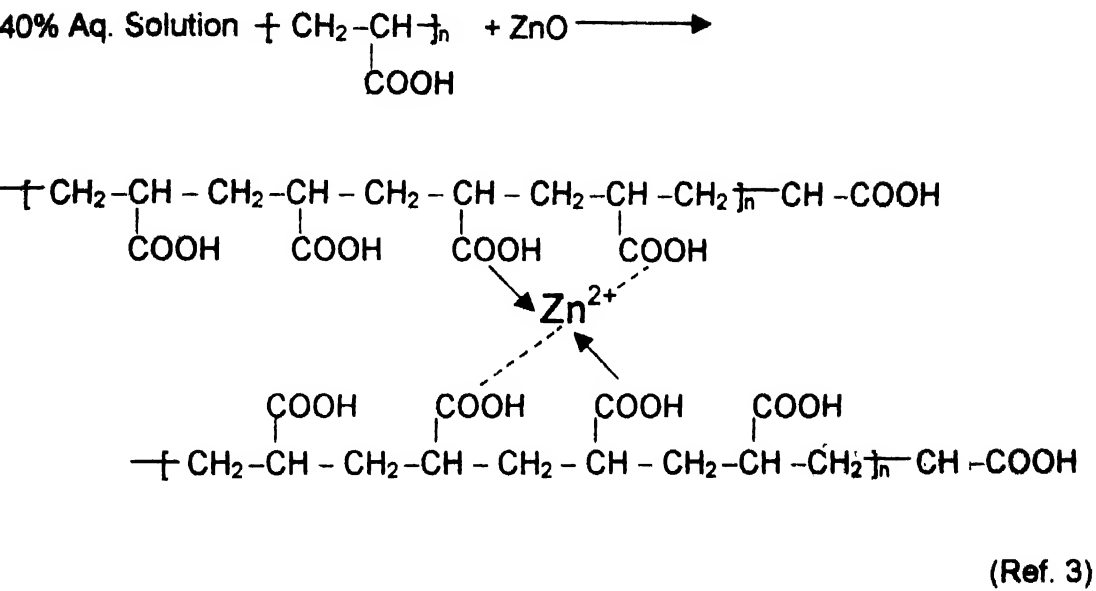
Scheme: Mechanism of hardening of ZnO and polyacrylic acid to
Zinc polyacrylate, also tooth enamel.

The adhesion of polycarboxylte cement to the tooth enamel is superior to any of the cements available. The adhesion of other cements is purely mechanical and need acid etching prior to cementation. The adhesion of

10

polycarboxylate cement arises from etching of the enamel by the polyacrylic acid providing an easily wettable porous surface amenable to mechanical interlocking with the hardened cement and formation of ionic bonds between the calcium and carboxylate ions at the resin enamel interface. The adhesion is good even after prolonged water exposure. The general biocompatibility of these materials is excellent. The compressive strength of these materials is reasonably high but lower than phosphate cements. The tensile strength is to some extent higher than phosphate cements.

Though polycarboxylate cement mix appears to be more viscous compared to other cements, still it flows under pressure to give a reasonable film thickness. The setting time is short. These materials have mild effect on the pulp. This is due to:

(a) rapid rise of setting cement towards neutrality,

(b) localization of the polyacrylic acid because of its molecular size,

(c) minimal movement of the fluid in the dentinal tubules.

The main advantages of these materials are excellent adhesion to the tooth enamel coupled with little pulp reaction. And the main disadvantage is that for attaining optimum properties, an accurate proportion of powder and liquid is essential and polycarboxylate cement has lower compressive strength and shorter working time than phosphate cements.

CHAPTER 2
EXPERIMENTAL DETAILS

2.1. MATERIALS:

Acrylic acid was polymerized to polyacrylic acid using potassium persulphate as initiator and isopropanol as chain transfer agent. Distilled water was used as a medium for solution polymerization. ZnO, which was deactivated, was used as the inorganic component (powder) of the poly-carboxylate cement. 2N NaOH was used as a solvent to dissolve the polyacrylic acid for the molecular weight determination.

2.2. PREPARATION OF POLYACRYLIC ACID:

A three necked round bottomed flask fitted with a burette, thermometer pocket and reflux condenser was taken and a magnetic stirrer was put inside it. 200 ml of distilled water and 2.4 gms of potassium persulphate $(K_2S_2O_8)$ were taken in the three necked round bottom flask. Two drops of isopropanol was added as chain transfer agent to control the molecular weight. The three necked round bottom flask was then put on the magnetic stirrer cum heat control device and the temperature was increased until a fixed temperature of 90°C was attained. Simultaneously the magnetic stirrer was on in order to dissolve the potassium persulphate $(K_2S_2O_8)$ initiator in the distilled water inside the three necked round bottom flask. While setting the temperature the mercury

12

tip of the thermometer was well dipped inside the solution and care was taken so that the mercury tip should not touch the base of the round bottom flask for the accurate measurement of the temperature. 50 ml of acrylic acid was taken in a burette, which was fitted with one of the necks of the three necked round bottom flask. When the fixed temperature (90°C) was attained, acrylic acid was added drop wise from the burette at a rate of 2 ml per minute with constant stirring. When 10 ml of acrylic acid was consumed from the burette, another 10 ml of previously measured acrylic acid was added into the burette as a total of 60 ml of acrylic acid was needed for the purpose and the burette capacity was only 50 ml. After the addition of acrylic acid was complete, the stirring was continued for another two hours at the fixed temperature of 90°C for complete polymerization. The mixture was gradually cooled to room temperature with stirring resulting in the formation of polyacrylic acid as a viscous aqueous solution. This was then concentrated at 50°C .The concentrated aqueous polyacrylic acid was precipitated by adding it to acetone taken in a beaker and stirring vigorously. The precipitate was decanted and was washed with acetone several times till no traces of unreacted acrylic acid was detected with alcoholic potassium permanganate ($KMnO_4$) solution for unsaturation (Bayer's test). The purple colour of $KMnO_4$ disappears if the test is positive. It was dried at 50°C for 6 hours. A 40% aqueous solution of the dried polyacrylic acid was prepared and was used for further dental cement preparation. Experimental conditions for the preparation of polyacrylic acid of desired molecular weight of 45,000 to 50,000 is given in Table 2.1.

2.3. DEACTIVATION OF ZINC OXIDE:

The inorganic component of polycarboxylate cement is Zinc Oxide. The reaction of commercial Zinc Oxide with polyacrylic acid is too vigorous and fails to yield the required cement. To avoid this, the commercial Zinc Oxide was deactivated. Zinc Oxide was taken in a silica crucible and was deactivated by heating it at 1000°C in a muffle furnace for 30 hours Heating this way yields sintered ZnO, which is also denser and more consolidated and of lower specific area than the original Zinc Oxide and these changes bring about the desired reduction in chemical reactivity. The yellow coloured cake so obtained was powdered in a mortar pestle and was passed through a 75μm sieve. This was the powder that was used for the preparation of polycarboxylate cement

TABLE: 2.1

Acrylic acid	60 ml
Distilled water	200 ml
Potassium Persulphate	2.4 grams
	(4% of acrylic acid v/v)
Temperature	90°C
Rate of addition of acrylic acid	2 ml / min

2.4. PREPARATION OF POLYCARBOXYLATE (CEMENT) COMPOSITE:

It is true that any cement composition needs two important ingredients as a powder and a liquid. In the case of dental polycarboxylate cement preparations the liquid is polyacrylic acid and the powder is deactivated Zinc Oxide.

A 40% aqueous solution of polyacrylic acid was carefully prepared. Now the viscous polyacrylic acid solution is fit for the dental cement composition. This 40% aqueous solution of polyacrylic acid was mixed with deactivated Zinc Oxide in a powder/liquid ratio of 1.5:1 (w/w) on a glass plate to make the polycarboxylate cement. The powder and liquid were mixed thoroughly with the help of a glass rod until a uniform paste was obtained. With time the paste gradually set and hardened to a solid mass.

2.5. CHARACTERISATION OF POLYACRYLIC ACID AND THE DENTAL CEMENTS:

The polyacrylic acid and the dental cement composition were characterized by the thermal analyses (TGA and DTA), IR Spectroscopy, X-Ray diffraction. Also the polyacrylic acid and the dental cement composition were individually characterized by molecular mass determination and Scanning electron Microscopy (SEM) respectively.

15

2.51. DETERMINATION OF MOLECULAR MASS OF POLYACRYLIC ACID:

The viscosity average molecular mass of prepared polyacrylic acid was determined. The solvent used for this purpose was 2N NaOH aqueous solution. Polyacrylic acid solution of 0.5% (gms /dl) was prepared by dissolving 0.5 grams of Polyacrylic acid in 100 ml of 2N NaOH. This solution was further diluted by adding the solvent to prepare solutions of three other concentrations i.e. 0.2%, 0.1% and 0.05 %. The solvent flow time (t_o) and the solution flow time (t) of all the four different concentrations were measured at room temperature (24^0C) using an Ostwald viscometer. The relative viscosities (η_r) were measured for each concentration. By calculating the inherent viscosities (ln η_r/C) at different concentrations, a plot of these was drawn against concentration of the polymer solution. The linear plot so obtained was extrapolated to zero concentration. The ordinate intercept of this graph gives intrinsic viscosity [η]. The Molecular mass was calculated by using the Mark Houwink's equation.

$$[\eta] = K \, \overline{M}^{\alpha}$$

Where K = 4.22×10^{-4}

α =0.64   (for 2N NaOH as solvent)

$\overline{M}$ = Average Molecular mass

[η]= Intrinsic Viscosity

For good performance of polycarboxylate cement the Molecular mass of 45,000 to 50,000 was desired.

2.52. IR Spectra:

The IR Spectra of Polyacrylic acid and Zinc Polycarboxylate cement was recorded in a Perkin-Elmer FTIR spectrometer in the range 400-4000cm^{-1} by using KBr pallet technique, in the University Science and Instrumentation Centre (USIC), University of Delhi, Delhi.

The IR Spectra was studied for the examination of double bond in the sample to confirm complete polymerization and the structure of Polyacrylic acid was also investigated.

2.53. THERMOGRAVIMETRIC ANALYSIS (TGA) and DIFFERENTIAL THERMAL ANALYSIS (DTA)

Simultaneously Thermo-gravimetric analysis (TGA) and Differential Thermal Analysis (DTA) were recorded using 10.8 mg sample in a platinum crucible at a heating rate of 10°C per minute on a Rigaco-8150 instrument at USIC, University of Delhi, Delhi. Alumina (Al_2O_3) was used as the reference material for DTA.

The DTA plot was studied to observe the endothermic and exothermic changes in the Polyacrylic acid sample with increasing temperature in order to ascertain the Tg and Tm and other thermal changes of Polyacrylic acid. The TG curve was investigated to observe the weight loss of Polyacrylic acid sample at various temperatures. From the weight loss data against temperature, the activation energy and Arrhenius factor and entropy change of thermal degradation of Polyacrylic acid was calculated by two different techniques

i.e. **(i) Sharp-Wentworth Method:**

for n=1 (first Order reaction)

$$\log \left[(dC/dT)\big/(1-C) \right] = \log(A/\beta) - (Ea/2\ 303R)(1/T)$$

Where

C (the fraction decomposed) = $(W_0 - W_T)\big/(W_0 - W_F)$

W_0 = Initial weight

W_T = weight at temperature T

W_F = Final weight

Ea = Activation energy

A = Arrhenius (frequency) factor

R = Universal gas Constant

18

(ii) Broido Method:

For n=1(first order reaction)

$$\ln [g(\alpha)] = \ln [A/\beta \times (R/Ea)(Tmax)^2] - [(Ea/R)(1/T)]$$

Where

Tmax = Temperature of maximum rate of weight loss

$g(\alpha)$ =The fraction decomposed (same as 'C' in Sharp-Wentworth method)

T_2 =Final temperature

Ea = Activation energy

R = Universal gas constant

2.54. X-Ray Diffraction Pattern:

The XRD pattern of both Polyacrylic acid and Zinc Polycarboxylate cement were recorded on a PHILLIPS PW-3710 X-Ray diffractometer, using Cu_α X–radiations of wave lengths 1.54056 Å and 1.54439 Å and a continuous scan of 3^0/min. The diffractometer was operated at 40 kV and 20 mA current. The diffraction pattern was studied for crystallinity. The crystallite size was determined by using *Scherrer formula.*

i.e. $L = \dfrac{0.9\lambda}{\Delta(2\theta)\cos\theta}$

Where

L= Coherence length (crystallite size)

λ =Wavelength of X-Ray radiation

$\Delta(2\theta)$ = Peak width

θ =Reflection angle

2.55. SCANNING ELECTRON MICROSCOPY (SEM):

Scanning Electron Microscopy is a valuable tool in ascertaining the surface morphology and microstructure of many materials. This technique provides the clear and magnified picture of the basic matrix and the reinforcement pattern in the polymeric systems. It also helps in identifying the development and propagation of cracks if any in a system. This technique involves viewing of a surface magnified several thousand times. The sample of polycarboxylate cement was prepared in P/L ratio of 1.5:1and examined under a scanning electron microscope (JEOL 840) with a magnification of 2500 times.

CHAPTER 3

EVALUATION OF POLYCARBOXYLATE CEMENT

Polycarboxylate dental cement was evaluated by several properties such as setting time, compressive strength and diametral tensile strength for evaluation as restorative material in dentistry.

3.1. SETTING TIME: Specimen Preparation and determination of Setting time

Setting time is defined as the period of time from the initiation of the mixing till the cement becomes brittle. Dental cements are required to set within a few minutes at oral temperature and harden rapidly. This property enables the dentist to trim and finish a restoration in a single session. It lessens the danger of displacing freshly cemented inlay or crown and reduces the risk of moisture damage to the vulnerable surface of hardening cement. This is dependent on the powder/liquid ratio, temperature as well as humidity.

For the measurement of setting time a metallic ring of dimensions 4.8 mm height, 11.1 mm outer diameter and 9.5 mm inner diameter was placed on a flat glass plate and was filled with a portion of freshly prepared cement (p/l ratio 1.5 : 1 w/w) which was prepared at 38^0C and 70% Relative humidity. Four

minutes after the starting of the mixing a standard Vicat needle weighing 6.9 grams was lowered on the cement sample that penetrates into it. The process was continued repeatedly in an interval of 30 seconds as long as the penetration of the needle more and more into the sample was observed. The setting time was noted as the time elapsed from the starting of the experiment until the needle fails to penetrate into the cement.

3.2. COMPRESSIVE STRENGTH AND DIAMETRAL TENSILE STRENGTH

The most important quality for a material is to possess its toughness i.e. its ability to absorb energy without fracturing. This parameter is difficult to measure in dental cements due to technical difficulties. Increased toughness can only be obtained at the expense of strength. There are two fundamental parameters of measuring strength such as tensile failure that occurs by the separation of planes and the shearing failure that occurs due to the sliding of planes one over the other.

Most common parameters of measuring the strength of dental cements are compressive strength and diametral tensile strength. The former is determined as the resistance to compression over a particular area. Dental cements are brittle in nature. So the conventional methods of testing dumb-bell shaped specimen for tensile strength does not hold good for these cements. However the tensile strength is measured under compression along the diametral axis (diametral compression method).

22

Zinc Phosphate cement has the highest strength amongst the Zinc Oxide based cements such as Polycarboxylate and Zinc Oxide-Eugenol cements. However the compressive strength is dependent on the powder/liquid ratio. Dental cements are always prepared with an excess of powder over liquid Normally only a fraction of powder is consumed in the cement forming reaction. Thus dental cements can be regarded as composite materials where the excess of unattacked powder acts as filler. The effect of powder/liquid ratio on compressive strength of Zinc Phosphate cement and Polycarboxylate cement is shown in figure 3.1.
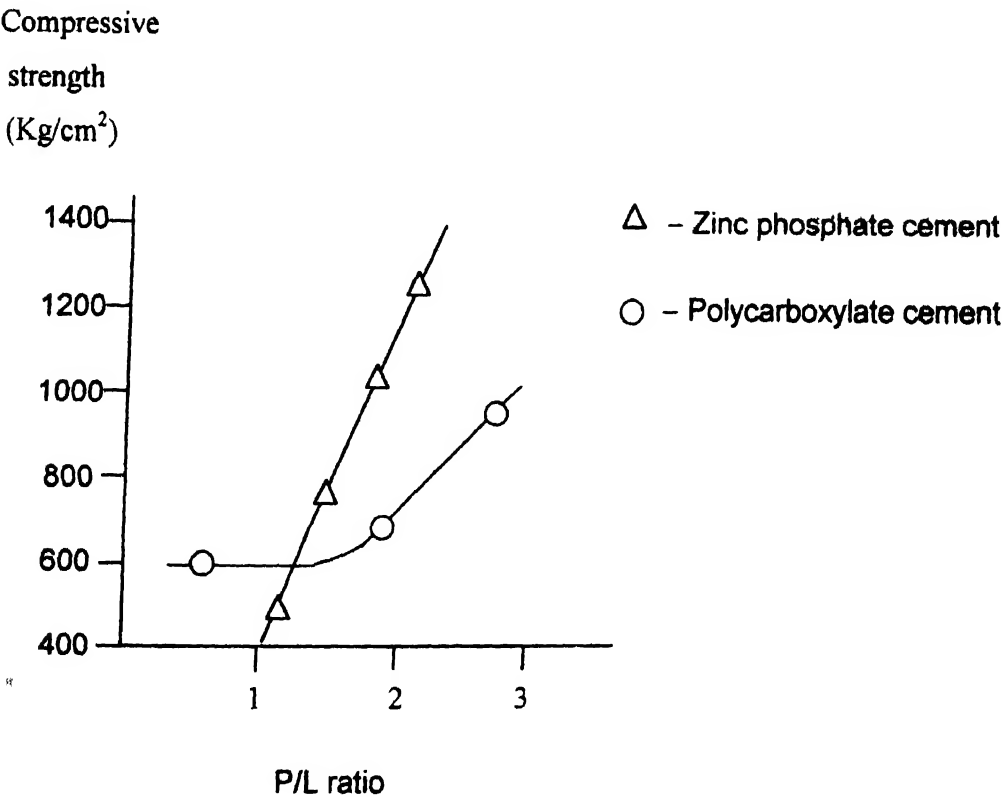
Compressive

strength

(Kg/cm^2)

FIG.3.1: Compressive strength of Zinc Phosphate cement and

Polycarboxylate cement against various P/L ratios.

23

It is obvious from the figure that in Zinc Phosphate the compressive strength increases sharply with increase in P/L ratio whereas in Polycarboxylate cement the increase is gradual.

3.21. Specimen Preparation and Determination Of Compressive strength:

For the determination of Compressive strength a specimen of 6mm diameter and 12mm height was prepared in a stainless steel split mould at 23.5^0C. The split mould was placed on a flat glass plate and was slightly overfilled with a portion of the standard mix of the cement within two minutes after commencing of the mix. A second plate was placed on the top of the mould and the plates were tightly pressed with a C-clamp.

An hour later the ends of the cylinder of cement was ground flat at right angles to the long axis by the use of a 240-grit Silicon Carbide paper. The test specimen was kept wet during the grinding and was rotated about a quarter turn for every few strokes. After grinding, the specimen was removed from the mould and was stored in distilled water for 23 hours. The Compressive Strength of the specimen was determined. The specimen was placed with the flat ends covered with wet filter paper between the platens of **Instron Universal Testing Machine** so that the load is applied along the long axis of the specimen. The crosshead speed of the device was 0.05 cm/min. The maximum load at which the specimen fractured was recorded. The Compressive Strength was calculated using the formula:

$$P = 4F \big/ \pi d^2$$

Where   P = Compressive Strength   (in Kg/cm^2)

         d= Diameter of the specimen   (in cm)

         F = Maximum applied load   (in Kg)

3.22. Specimen Preparation and Determination Of Diametral Tensile Strength:

       Specimen preparation for the determination of Diametral Tensile Strength was prepared in the same manner and the size of the specimen was the same as those of used for Compressive strength determination   For the determination of Diametral Tensile strength the specimen was placed with the diametral surfaces covered with a piece of wet filter paper between the platens of the testing machine so that the load is applied along the short axis of the specimen. The maximum load where the specimen fractured was recorded. The Diametral Tensile Strength was calculated from the following formula.

$$T = 2F \big/ \pi l d$$

Where   T = Diametral Tensile Strength   (in Kg/cm^2)

         F = Maximum load (in Kg)

         l= Length of specimen (in cm)

         d= Diameter of specimen (in cm)

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Polyacrylic Acid:

The organic component of the Polycarboxylate cement i.e. Polyacrylic Acid was characterized by various parameters such as Molecular mass , Infra Red Spectroscopy, Thermogravimetric analysis, differential thermal analysis as well as X-Ray Diffraction studies which are discussed below.

4.11. Molecular Mass:

The flow time of the solvent (2N NaOH) and polyacrylic acid at various concentrations were measured by using Ostwald viscometer, which are given in table 4.1.

The Molecular mass was determined by using the Mark Houwink's equation.

i.e. $[\eta] = K \overline{M}^{\alpha}$

Where K (Constant when NaOH is the solvent) = 4.22×10^{-4}

$\alpha = 0.64$

$\overline{M}$ = Average molecular mass.

$[\eta]$ = Intrinsic Viscosity

The value of the Intrinsic Viscosity [η], which was taken from the plot by extrapolating to zero concentration, given in figure 4.11, was used to calculate the Molecular Mass. The Intrinsic Viscosity at zero concentration was found to be 0.425. From this the Molecular Mass was calculated from Mark-Hownik's equation.

Calculation of molecular   Mass:

$0.425 = 4.22 \times 10^{-4} \times \overline{M}^{0.64}$

$\overline{M}^{0.64} = 0.425/4.22 \times 10^{-4}$

$\overline{M}^{0.64} = 1007.109$

$\overline{M} = (1007.109)^{1/0.64}$

$\overline{M} = 49238.747$

OR $\overline{M} = 49239$

From the calculation, the Molecular Mass was found to be 49239.

Table 4.1

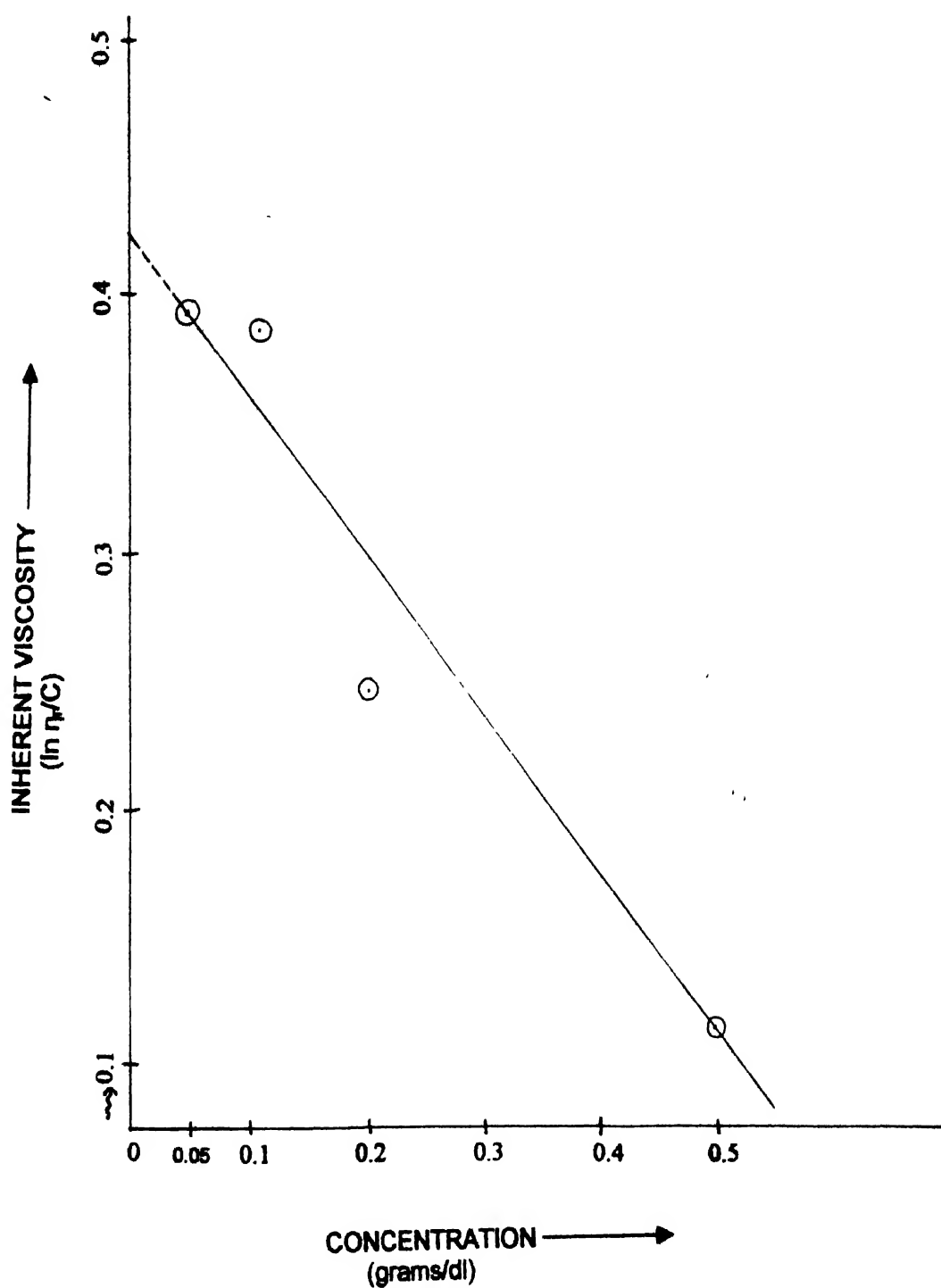| Solvent (2N NaOH) flow time = 101 sec.	
Concentration of Polyacrylic acid (g/dl)	Flow time (sec)
0.05	103
0.1	105
0.2	106
0.5	107

FIGURE: 4.11.   PLOT OF INHERENT VISCOSITY ($\ln \eta_r/C$) AGAINST
                 CONCENTRATION OF POLYACRYLIC ACID

4.12: Infrared analysis of Polyacrylic acid

The Infrared spectra of polyacrylic acid are shown in fig.4 12. From the critical analysis of this spectrum it was found that there is no peak in the region 1680 cm^{-1} to 1625 cm^{-1} which confirms the absence of C=C stretching, and further confirms complete polymerization of acrylic acid. Again the peaks at 1171.5 cm^{-1} to 850 cm^{-1} can be assigned to the open chain C–C stretching in the polymer moiety. The peak around 3300 cm^{-1} can be assigned to O–H stretching arises due to the presence of moisture in the system. The area registered at 2933.5 cm^{-1} can be assigned to the aliphatic C–H bending frequencies. The peak observed at 1731.5 cm^{-1} is due to C=O stretching of the carboxylic acid group.

4.13. DTA of Polyacrylic acid

A differential thermo gram (DTA curve) of Polyacrylic acid is shown in Fig.4.13. The first peak appeared in the thermogram at 102^0 C, can be assigned to the Glass transition temperature (Tg) of Polyacrylic acid. When Polyacrylic acid is heated above 200^0 C the endothermic peak observed at 214^0 C is due to the melting of Polyacrylic acid. The peak at around 261^{0}C is due to the liberation of a small amount of water to form anhydro-Polyacrylic acid consisting mainly of six membered rings resulting in de-polymerisation and cross linking. On further heating the anhydride starts to decompose and heating at about 400^{0}C results in

rapid decomposition to CO_2 and volatile hydrocarbons. The various endotherms observed are listed in table 4.2.

4.14. Thermo Gravimetric Analysis (TGA) of Polyacrylic acid

A typical TGA curve for Polyacrylic acid in air is given in figure 4.15. The degradation of the polymer was observed between 252^0C to 314^0C. The weight loss could be due to chain scission resulting from oxidation and char formation.

Activation Energy (Ea), Arrhenius (frequency) factor (A) and Entropy change (ΔS) were calculated by two different methods

(i) Sharp-Wentworth Method

For n=1 (first Order reaction)

$$\log [(dC/dT)/(1-C)] = \log(A/\beta) - (Ea/2.303R)(1/T)$$

From the weight loss data the values of C (the fraction decomposed) were calculated by using the formula

$$C = (W_0 - W_T)/(W_0 - W_F)$$

A plot   given   in the figure   was drawn taking

$\log [(dC/dT)/(1-C)]$ in the ordinate and $1/T$ in K^{-1} in the abscissa.

From the plot the slope was calculated and the intercept was taken by extrapolating to zero. The Activation Energy (Ea), Arrhenius Factor (A), change in Entropy (ΔS) of the thermal degradation of Polyacrylic acid were calculated. The Entropy change (ΔS) was calculated by using the formula:

$$A = (k\, T_{max}\, /\, h)(e^{\Delta S/ R})$$

Where   k= Boltzman's constant (0.32944×10^{-23} cal K^{-1})

          h= Planck   constant (1.5836×10^{-34} cal S)

The results are given in table 4.3.

(ii) Broido Method

For n=1(first order reaction)

$$\ln [g(\alpha)] = \ln [A/\beta \times (R/Ea)(Tmax)^2] - [(Ea/R)(1/T)]$$

The value of g (α), same as 'C' in the Sharp-Went Worth method was calculated from the weight loss data. 'Tmax' i.e. temperature of maximum rate of weight loss was found to be 544 K (271°C) which was used in the equation to calculate the Arrhenius factor from the intercept

A plot was drawn by taking ln [g(α)] in the ordinate against 1/T (in K^{-1}) in the abscissa.

The slope was calculated and the ordinate intercept was taken by extrapolating to zero.

The Activation energy (Ea), Arrhenius factor (A) and change in Entropy (ΔS) was calculated which are given in the table 4.3

31

TABLE: 4.2

DTA peaks of Polyacrylic acid

Peaks	Temperature (^{0}C)	Changes observed
Endo	102	Tg
Endo	214	Tm
Endo	261	Anhydride formation causing de-polymerisation and commencing of cross linking
Endo	400	Rapid decomposition

TABLE: 4.3

Activation energy (Ea), Arrhenius factor (A), and Entropy change (ΔS) of degradation of Polyacrylic acid as calculated.

	Sharp Went-Worth method	Broido method
Activation Energy (Ea) (Kcal/mol)	8.928	3.406
Arrhenius Factor (A) (min^{-1})	8.41×10^1	1.56×10^4
Change in entropy (ΔS) (Cal K^{-1} mol^{-1})	−59.06	−48.68

MEASUREMENT CONDITIONS FOR TG and DTA of POLYACRYLIC ACID

1) SAMPLE NAME   : PAA

2) SAMPLE WEIGHT   mg : 10.0

3) TEMPERATURE AREA (T_1, T_2)   deg : 0 , 500

4) RATE   deg/min : 10

5) SAMPLING TIME   sec : 2

6) TG RANGE   mg : 20

7) DTA RANGE   +/- microv : 100

Weight loss (%)	Temperature (^{0}C)	$1/K \times 10^3$
3.00	146.90	2.3810
6.00	227.60	1.9972
9.00	252.98	1.9009
12.00	271.20	1.8372
15.00	289.40	1.7778
18.00	314.88	1.7008
21.00	351.63	1.6007
24.00	390.28	1.5074
27.00	422.27	1.4381
30.00	447.99	1.3868
33.00	502.74	1.2889

33

PERKIN ELMER

42.00
%T

0.00

cm⁻¹

4000 3500 3000 2500 2000 1500 1000 500

2933.5
2122.5
1731.5
1562.4
1403.5
1171.5
722.0
491.9
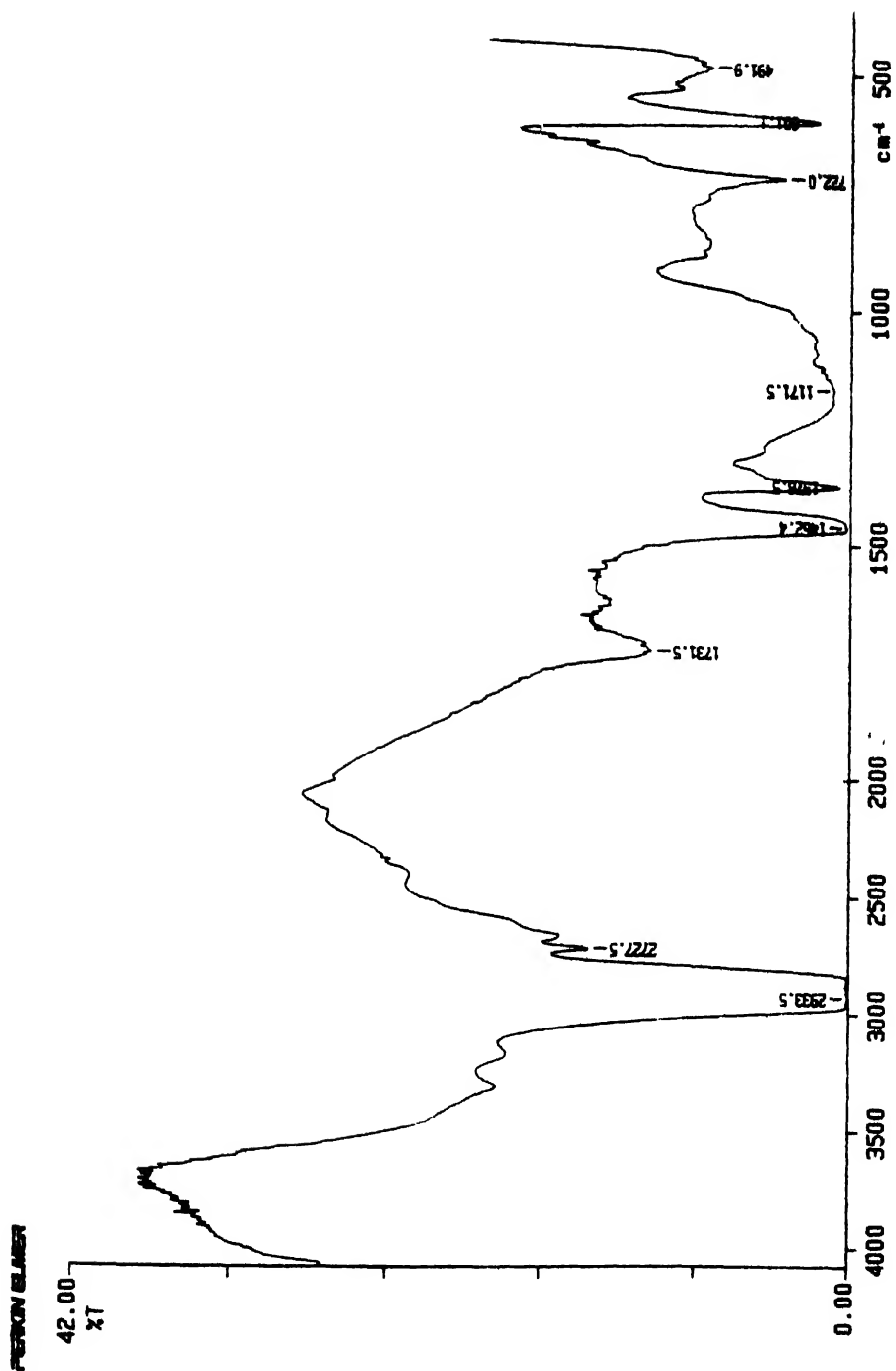
02/04/04 12:27 USIC DEL.UNIVERSITY
X: 1 scan, 4.0cm⁻1
PAA SCANNED BY S.K. SHARMA
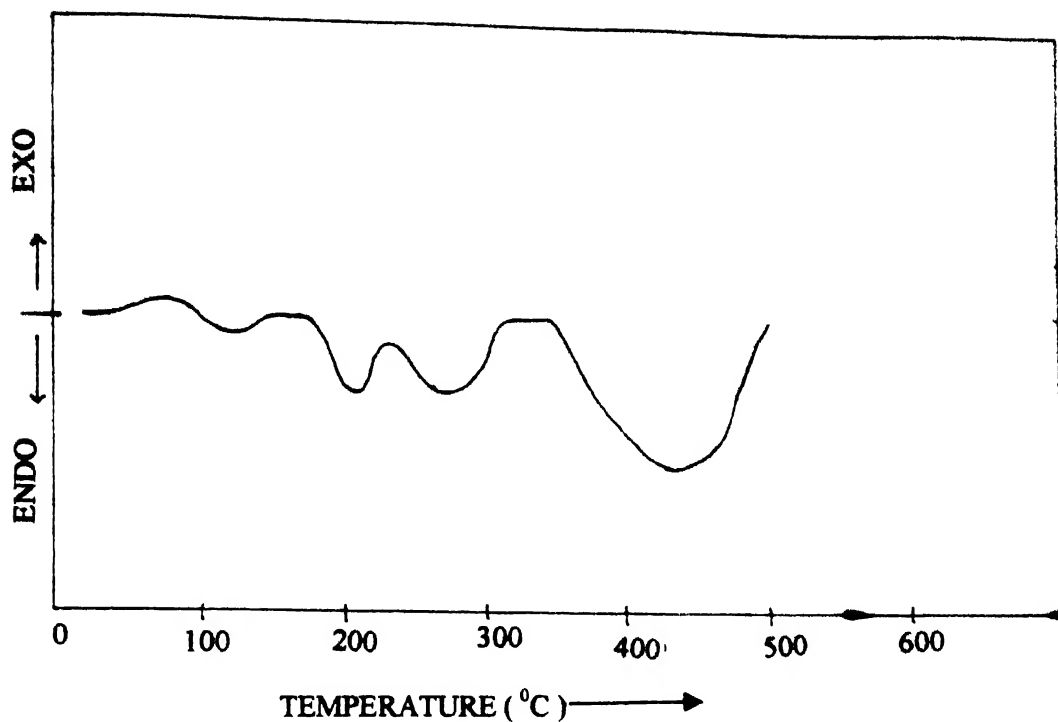
FIGURE: 4.12.   INFRARED SPECTRA OF POLYACRYLIC ACID

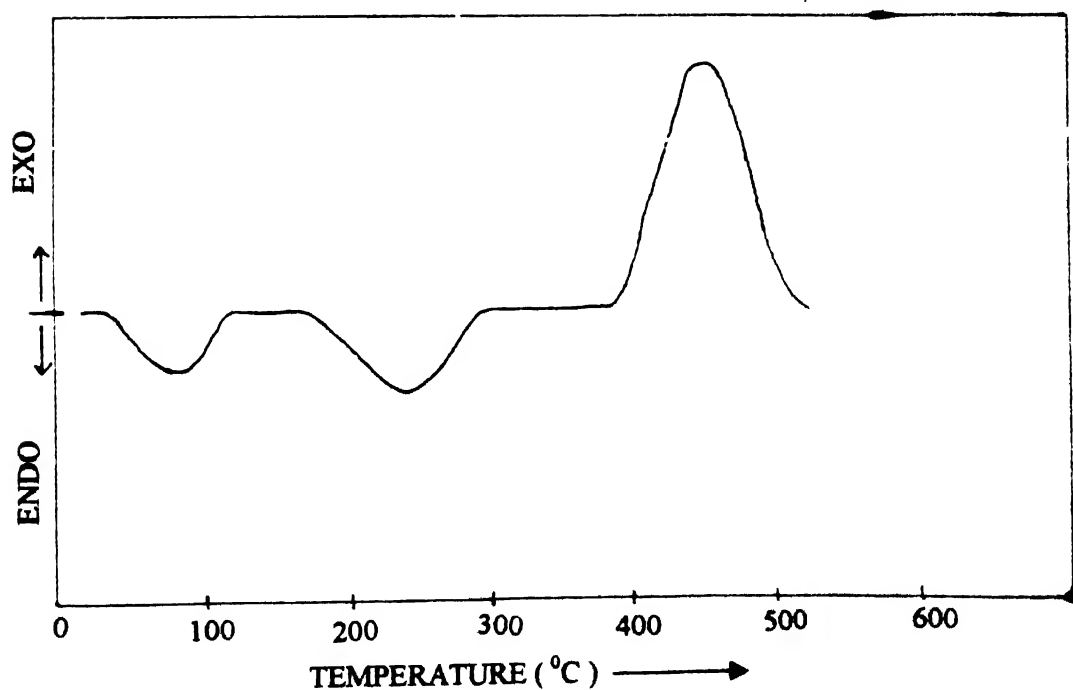FIGURE: 4.13.   DTA CURVES OF POLYACRYLIC ACID

FIGURE: 4.14.   DTA CURVES OF POLYCARBOXYLATE CEMENT

35
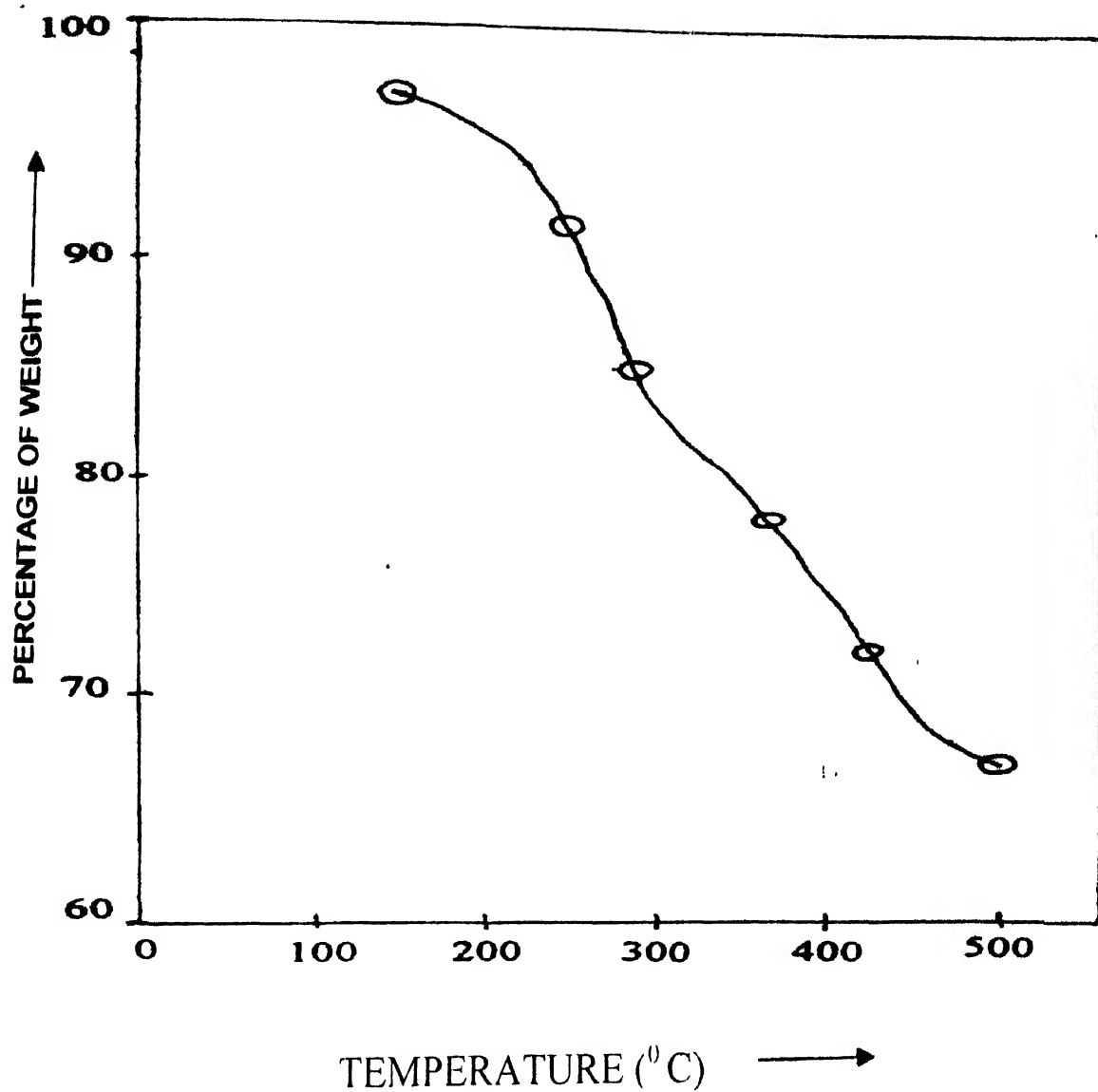
FIGURE: 4.15. TG CURVES OF POLYACRYLIC ACID

4.15: X-Ray Diffraction

X-Ray diffraction pattern of Polyacrylic acid shows a few significant peaks at Bragg's angle (2θ); 21.54^0, 30.06^0, and 30.93^0 A few small peaks were also observed at (2θ); 37.29^0, 40.59^0, and 43.61^0, which confirms some degree of crystallinity in Polyacrylic acid.

The peak having relative intensity 100% is at (2θ) 30.93^0, which corresponds to the d-spacing 2.8883 Å.

From the peak width (2θ) the coherence length (crystallite size) (L) of the crystalline order in the sample is calculated using Scherrer formula.

i.e. $L = 0.9\ \lambda / \Delta(2\theta)\ \text{Cos}\theta$

Where

L= Coherence length (crystallite size)

λ =Wavelength of X-Ray radiation

$\Delta(2\theta)$ = Peak width of the most intense peak

θ =Reflection angle

Here using λ= 1.54056 Å

$\Delta(2\theta)$ = 0.240

and $\theta = 2\theta/2 = 30.935/2 = 15.467$
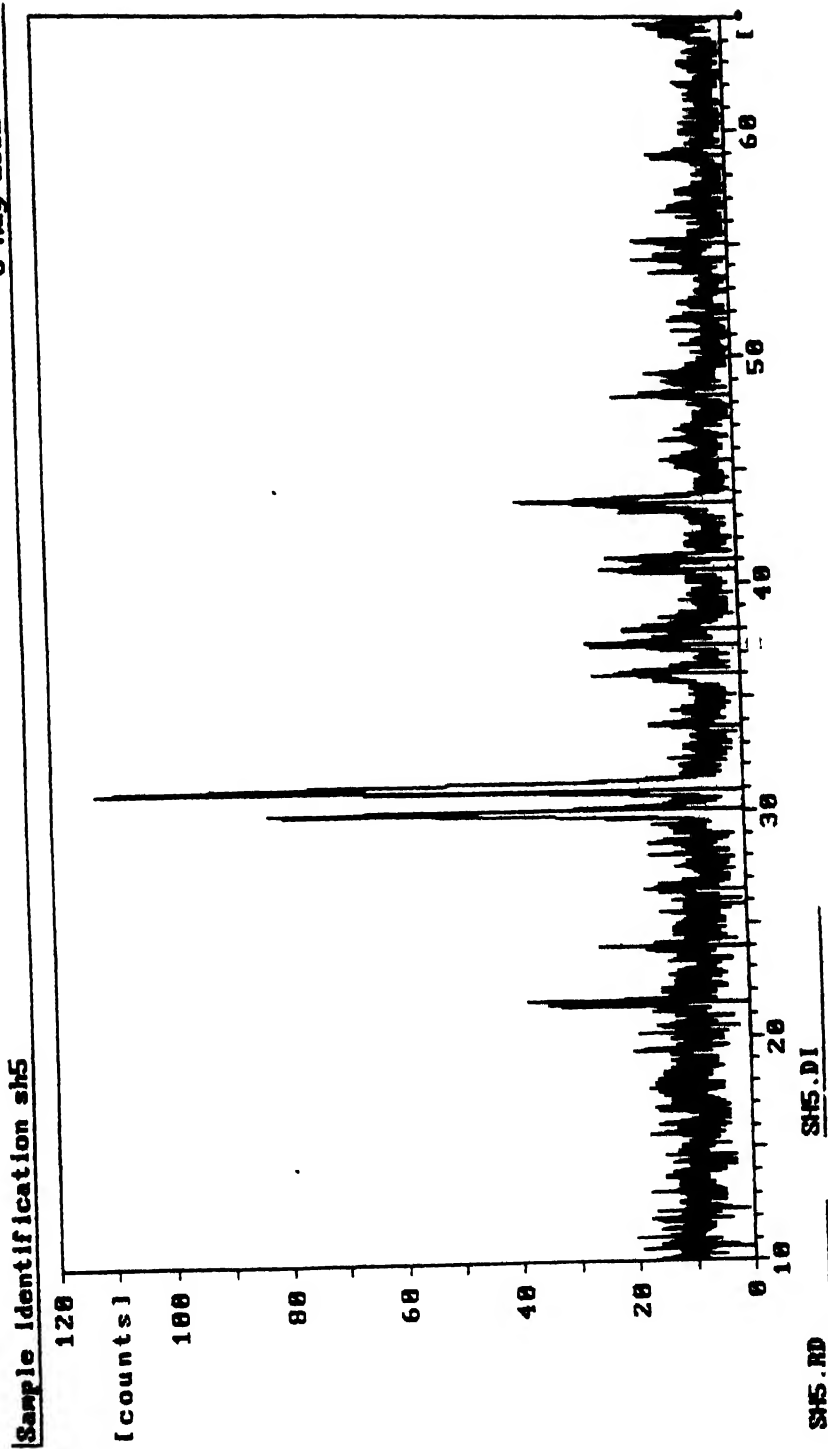
FIGURE: 4.16.   X-RAY DIFFRACTION PATTERN OF POLYACRYLIC ACID

File: SH5.DI

===

Philips Analytical X-Ray B.V.   PC-APD, Diffraction software

Sample identification: sh5
Data measured at: 6-May-2002 12:11:00

Diffractometer type: PW3710 BASED
Tube anode: Cu
Generator tension [kV]:   40
Generator current [mA]:   20
Wavelength Alpha1 [Å]:   1.54056
Wavelength Alpha2 [Å]:   1.54439
Intensity ratio (alpha2/alpha1): 0.500
Divergence slit: 1°
Receiving slit: 0.1
Monochromator used: NO

Start angle [°2θ]:   10.010
End angle [°2θ]:   64.990
Step size [°2θ]:   0.020
Maximum intensity: 82.8100
Time per step [s]:   0.200
Type of scan: CONTINUOUS

Peak positions defined by: Minimum of 2nd derivative of peak
Minimum peak tip width: 0.00
Maximum peak tip width: 1.00
Peak base width: 2.00
Minimum significance: 0.75
Number of peaks: 21

Angle [°2θ]	d-value α1 [Å]	d-value α2 [Å]	Peak width [°2θ]	Peak int [counts]	Back. int [counts]	Rel. int [%]	Signif.
10.655	8.2961	8.3167	0.960	0	10	0.4	2.15
21.540	4.1221	4.1323	0.080	20	8	24.5	0.90
23.970	3.7094	3.7186	0.320	10	7	12.4	1.21
26.490	3.3620	3.3703	0.320	5	6	6.4	0.91
30.060	2.9703	2.9777	0.140	49	7	59.2	0.89
30.935	2.8883	2.8955	0.240	83	7	100.0	3.56
33.750	2.6535	2.6601	0.320	2	5	2.7	0.79
36.055	2.4890	2.4952	0.400	12	5	14.8	2.10
37.295	2.4090	2.4150	0.320	18	5	21.3	3.59
37.970	2.3678	2.3736	0.240	11	4	13.2	1.31
40.595	2.2205	2.2260	0.280	18	4	22.3	2.44
41.060	2.1964	2.2019	0.200	12	4	14.8	1.25
43.610	2.0737	2.0789	0.160	26	4	31.4	1.34
45.470	1.9931	1.9981	0.480	4	3	5.3	1.11
48.330	1.8816	1.8863	0.320	10	3	11.6	1.61
51.670	1.7676	1.7720	0.240	5	2	5.8	1.69
54.395	1.6853	1.6895	0.240	8	2	9.5	1.14
55.055	1.6666	1.6708	0.240	11	2	13.2	1.59
56.560	1.6258	1.6299	0.240	5	2	6.4	1.22
57.255	1.6077	1.6117	0.240	4	2	4.8	0.91
58.840	1.5681	1.5720	0.480	5	3	5.8	0.79

The value of the crystallite size (L) of the polyacrylic acid calculated in this way was found to be 5.994Å.

4.2: Polycarboxylate cement

4.21: Infra Red spectra of Polycarboxylate cement

The Infrared spectra of Polycarboxylate cement are shown in figure 4.21. As the cement is set due to the reaction between Polyacrylic acid and Zinc Oxide (a basic oxide), so the area of our interest is concentrated on the type of bond formed between the Zn^{2+} ion and the carboxylic groups of the polymer acid.

The assignment of spectral bands is complicated because of the polymeric nature of the material. Being a polymer, it is unlikely to consist of discrete entities of the type found in, for example, the crystalline zinc carboxylates

The five most likely modes of bonding, which can be exhibited by carboxylate groups, as described by different authors are given in figure 4.22. These are (A) Ionic, (B) bridging bidentate, (C) chelating bidentate, (D) the asymmetric unidentate which is predominantly co-valent, (E) an eight membered metal chelate ring with a ligand that is essentially $-OOC-CH-CH_2-CH-COO-$

PERKIN ELMER

50.17
%T

42

1.58
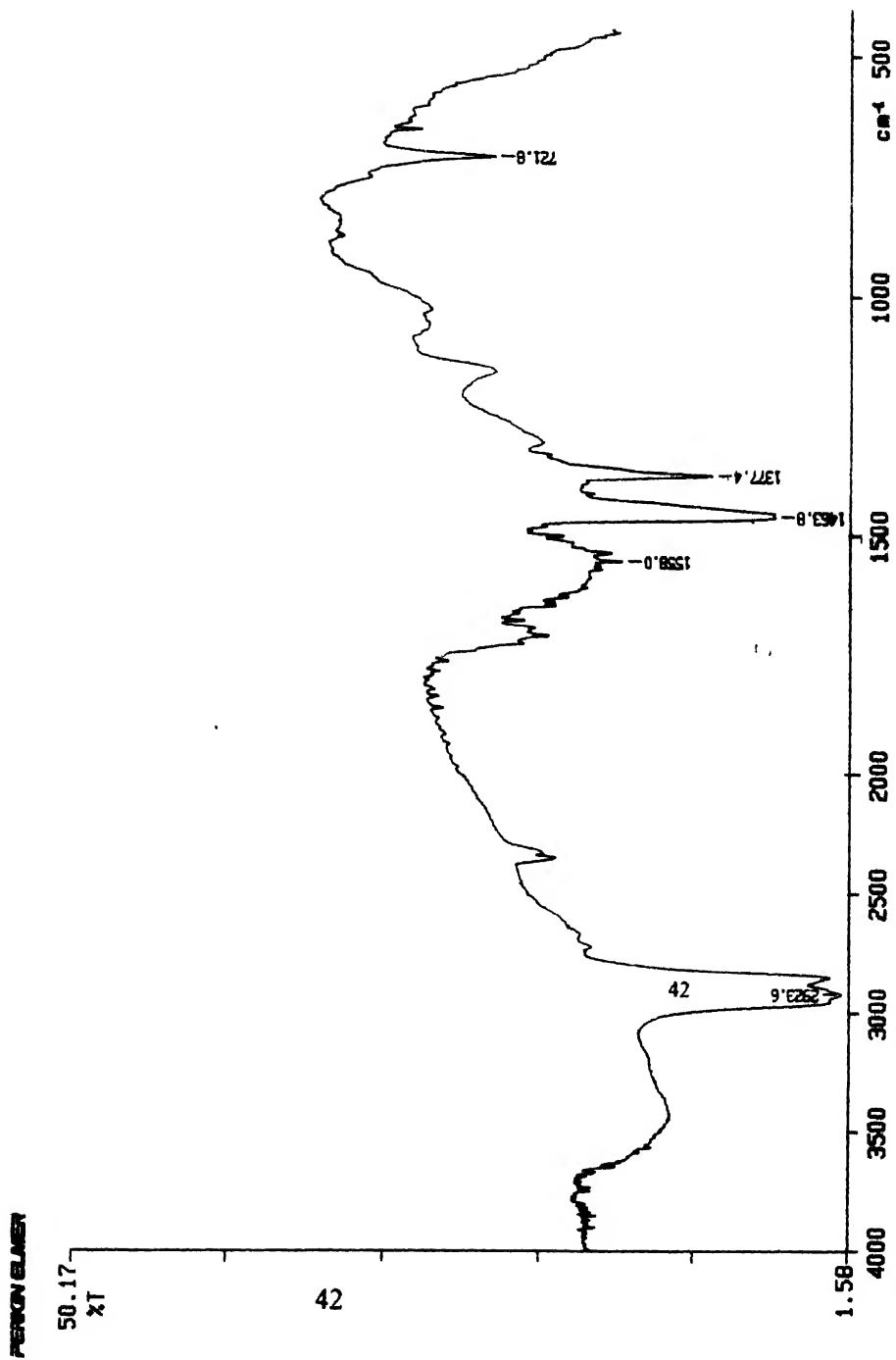
02/06/05 16:26 USIC DEL.UNIVERSITY
Y: 1 scan, 4.0cm-1
SAMPLE NO P

721.8
1377.4
1463.8
1558.0
2923.6
42
4000 3500 3000 2500 2000 1500 1000 500   cm⁻¹

(A) IONIC

(B) BRIDGING BIDENTATE

(C) CHELATING BIDENTATE

(D) ASYMMETRIC UNIDENTATE

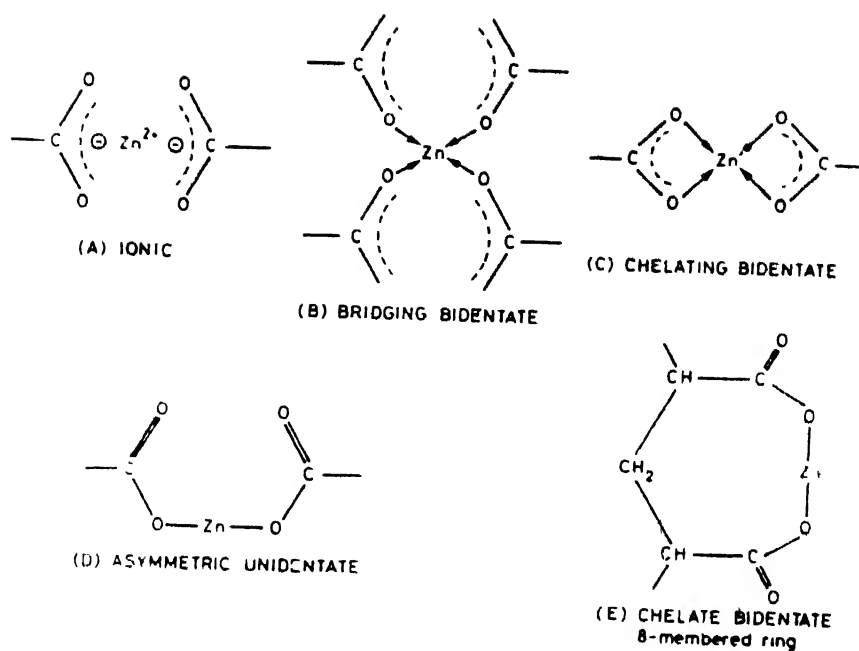(E) CHELATE BIDENTATE
8-membered ring

FIGURE: 4.22.　FIVE MOST LIKELY MODES OF BONDING EXHIBITED BY
CARBOXYLATE GROUPS.
(A) Ionic, (B) bridging bidentate, (C) chelating bidentate, (D) the
asymmetric unidentate which is predominantly co-valent, (E) an eight
membered metal chelate ring.

Bridging carboxylates give a band at about 1600 cm^{-1}, ionic species at about 1562 cm $^{-1}$, and chelating carboxylates at around 1550 cm^{-1}. For example in diacetatobisaquazinc (II) the band comes at 1550 cm^{-1}.

Comparing the IR spectra of the polycarboxylate cement with the spectra obtained for polyacrylic acid it is found that a broad band containing many small peaks is registered at 1558 cm^{-1}.

From the critical analysis of the spectrum around that region it can be ascertained that the peak at 1558 cm^{-1} is most intense which confirms the bonding type is predominantly ionic. The small bands around the region 1600cm^{-1} might be due to the formation of bridging (bidentate) carboxylates to some extent and the peaks around 1540 cm^{-1} to 1550 cm^{-1} can be assigned to the formation of a small amount of chelating carboxylates as given in structures B and C respectively in figure 4.22.

The presence of a small peak at around 1730 cm^{-1} indicates the presence of a small amount of residual acid, which probably failed to bond with the Zn^{2+} ions.

4.22: TG of Polycarboxylate cememt

The TG thermogram of polycarboxylate cement is shown in figure 4.23. From the curve it is indicated that the sample lost 4% of its initial weight upto 150^{0}C. This

may be attributed to the loss of water. Then a rapid weight loss occurred between 350°C to 450°C, which is assigned to the breakdown of the Zinc Polyacrylate.

The Activation energy (Ea), Arrhenius factor (A) and Entropy change (ΔS) was calculated by using Broido method using the same formula as used in case of Polyacrylic acid. The results are given in table 4.4.

TABLE: 4.4

Activation energy (Ea), Arrhenius factor (A) and Entropy change (ΔS) of degradation of Polycarboxylate cement as calculated by Broido method.

Activation Energy (Ea) (Kcal/mol)	2.384
Arrhenius Factor (A) (min^{-1})	1.38×10^7
Change in entropy (ΔS) (Cal K^{-1} mol^{-1})	−35 718

MEASUREMENT CONDITIONS FOR TG and DTA of POLYCARBOXYLATE CEMENT

1) SAMPLE NAME : PAAC

2) SAMPLE WEIGHT mg : 25.9

3) TEMPERATURE AREA (T_1, T_2) deg : 0, 600

4) RATE deg/min : 10

5) SAMPLING TIME sec : 2

6) TG RANGE mg : 50

7) DTA RANGE +/- microv : 100

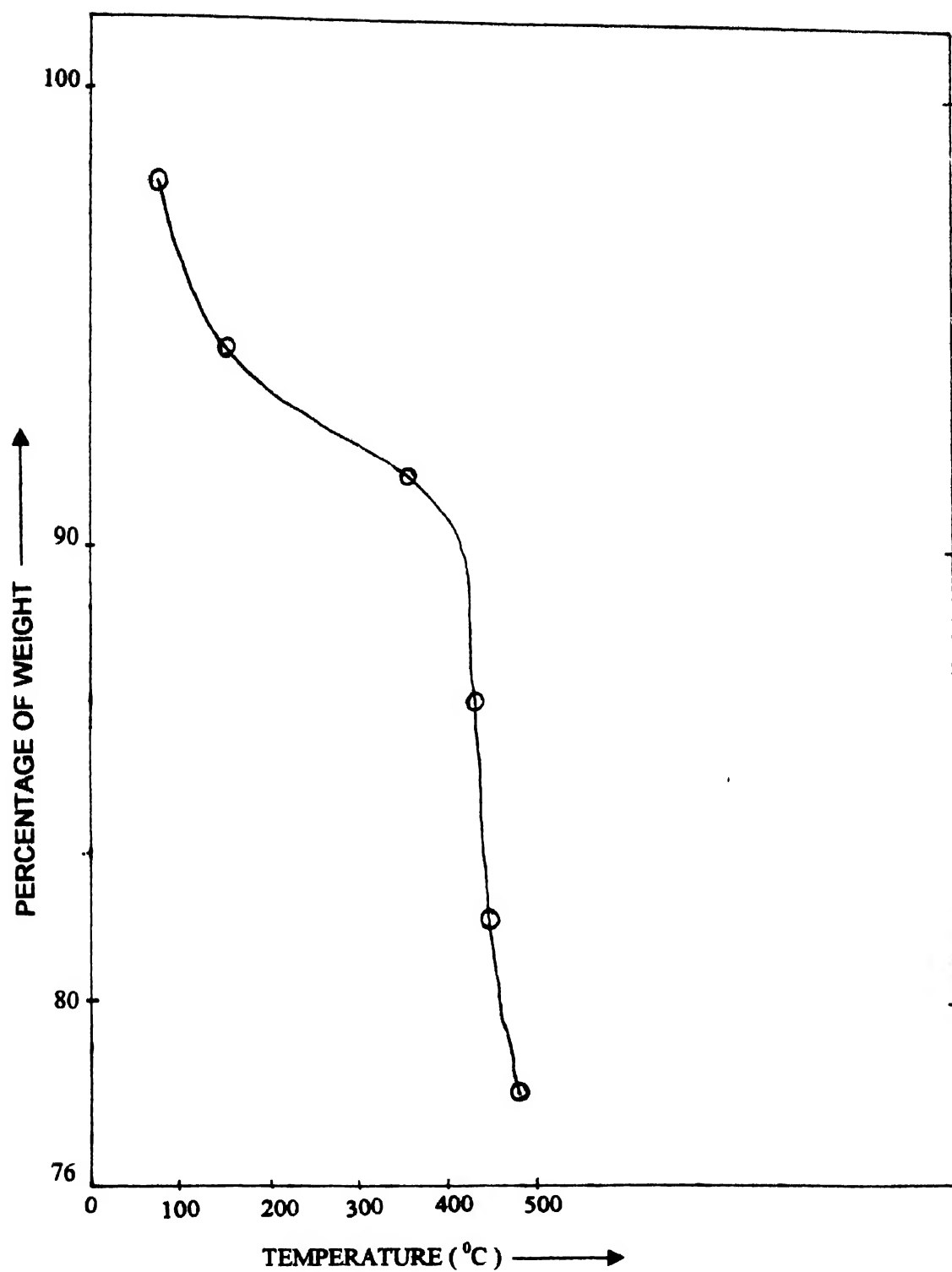| Weight loss (%)	Temperature (^{0}C)	$1/K \times 10^3$
2.00	74.79	2.8745
4.00	108.12	2.6232
6.00	168.65	2.2637
8.00	322.06	1.6802
10.00	420.80	1.4411
12.00	429.56	1.4232
14.00	434.41	1.4134
16.00	440.40	1.4015
18.00	446.93	1.3888
20.00	458.11	1.3676
22.00	481.25	1.3256

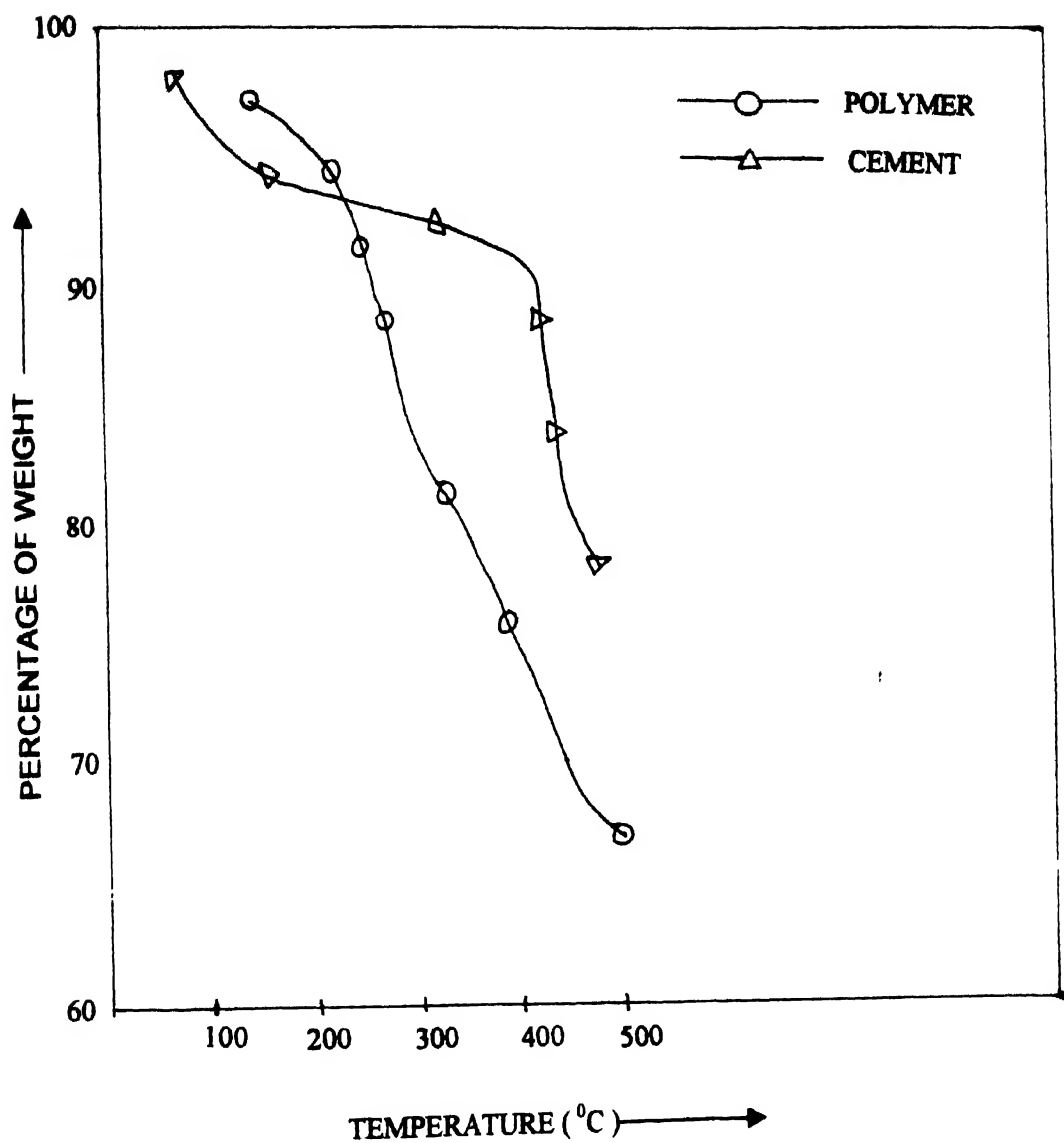FIGURE. 4.23.   TG CURVES OF POLYCARBOXYLATE CEMENT

FIGURE 4.24 A COMPARISION OF TG CURVES OF POLYACRYLIC ACID
AND POLYCARBOXYLATE CEMENT

4.23: DTA of Polycarboxylate cememt

From the DTA thermogram of Polycarboxylate cement the peaks are shown in figure 4.14 and listed in table 4.5. The endothermic peak at 81^0C can be assigned to the water loss that might be due to the moisture absorbed during storage. When heated above 200^0C, the commencing of the broad peak at 240^0C is due to the melting of the composite. The intense exothermic peak at 450^0C is due to combustion of the Polycarboxylate cement.

Table: 4.5

DTA peaks of Polycarboxylate cement

Peaks (Endo / Exo)	Temperature (^0C)	Changes observed
Endo	81^0C	Water loss
Endo	240^0C	Melting of the composite
Exo	450^0C	Combustion

6-Jun-2002 1

[counts]
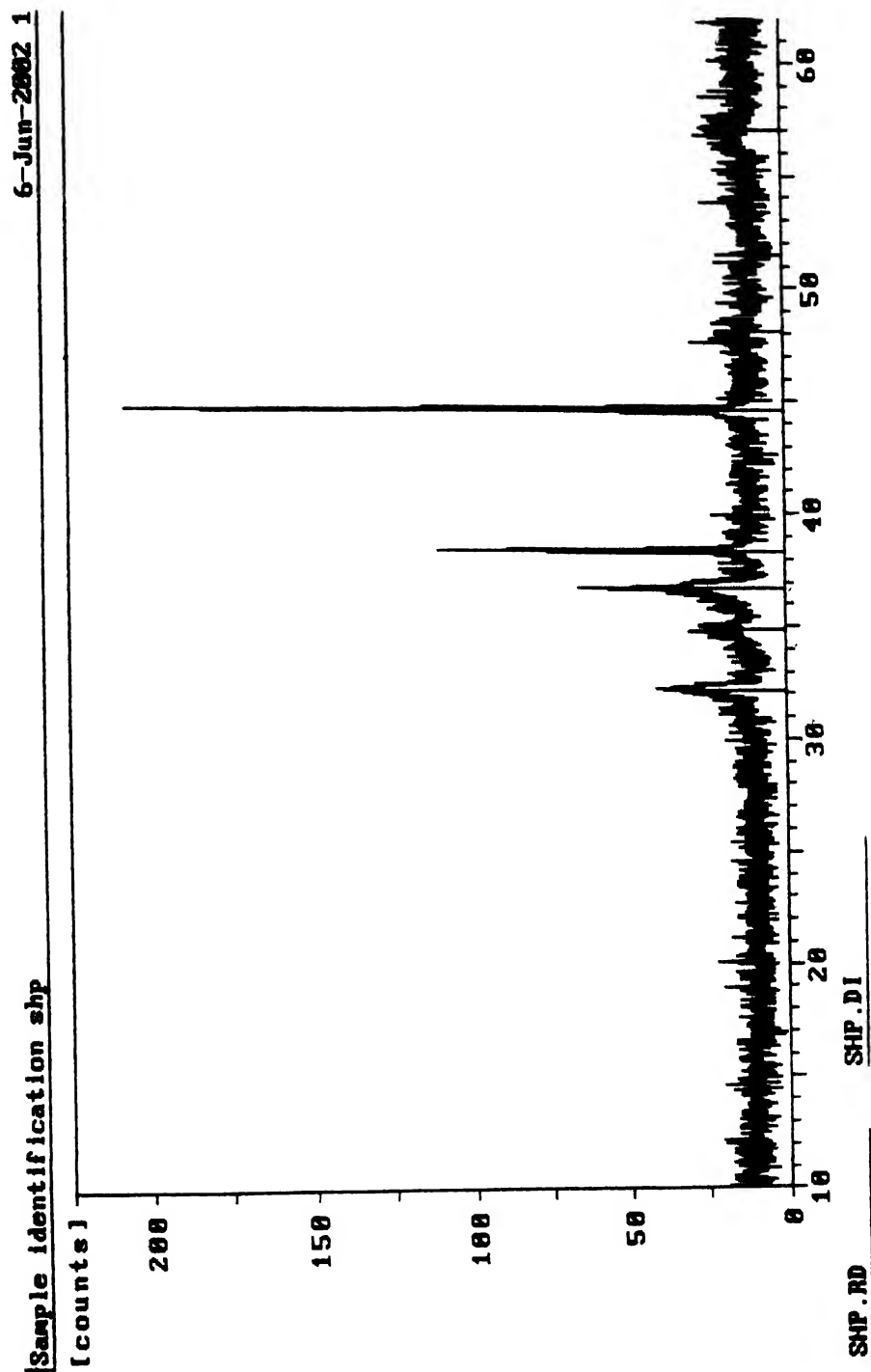
FIGURE: 4.25   X-RAY DIFFRACTION PATTERN OF POLYCARBOXYLATE
CEMENT

SHP.DI

SHP.RD

50

File: SHP.DI

==

Philips Analytical X-Ray B.V.   PC-APD, Diffraction software

Sample identification: shp
Data measured at: 6-Jun-2002 13:09:00

Diffractometer type: PW3710 BASED
Tube anode: Cu
Generator tension [kV]: 40
Generator current [mA]: 20
Wavelength Alpha1 [Å]: 1.54056
Wavelength Alpha2 [Å]: 1.54439
Intensity ratio (alpha2/alpha1): 0.500
Divergence slit: 1°
Receiving slit: 0.1
Monochromator used: NO

Start angle [°2θ]: 10.010
End angle [°2θ]: 64.990
Step size [°2θ]: 0.020
Maximum intensity: 196.0000
Time per step [s]: 0.200
Type of scan: CONTINUOUS

Peak positions defined by: Minimum of 2nd derivative of peak
Minimum peak tip width: 0.00
Maximum peak tip width: 1.00
Peak base width: 2.00
Minimum significance: 0.75
Number of peaks: 9

51

Angle [°2θ]	d-value α1 [Å]	d-value α2 [Å]	Peak width [°2θ]	Peak int [counts]	Back. int [counts]	Rel. int [%]	Signif.
32.155	2.7814	2.7883	0.320	24	10	12.3	1.41
34.845	2.5726	2.5790	0.480	11	10	5.6	0.89
36.700	2.4467	2.4528	0.120	40	10	20.3	1.15
38.325	2.3466	2.3525	0.100	100	10	51.0	2.53
44.575	2.0310	2.0361	0.080	196	11	100.0	2.01
48.045	1.8921	1.8968	0.960	4	10	2.0	1.37
51.505	1.7729	1.7773	0.120	8	10	4.0	0.84
57.005	1.6142	1.6182	0.240	11	11	5.6	1.17
63.425	1.4654	1.4690	0.800	7	13	3.4	1.31

4.24: X-Ray diffraction pattern

The X-Ray diffraction pattern of Polycarboxylate cement is shown in figure 4.25. From the X-Ray diffraction pattern of Polycarboxylate cement, a few intense peaks were observed at Bragg's angle (2θ) 44.575^0 and 38.325^0 along with a few small peaks at 36.7^0 and 32.15^0, which indicates the crystallinity of the cement

The peak with relative intensity 100% is at (2θ) $44\,575^0$, which corresponds to the d-spacing 2.0310 Å

From the peak width (2θ) the coherence length (crystallite size) (L) of the crystalline order in the sample was calculated using *Scherrer* formula.

The value of the crystallite size (L) calculated in this way was found to be 18.73 Å.

4.25: SCANNING ELECTRON MICROSCOPY (SEM)

The SEM photographs indicate the clear view of the polymeric matrix and the reinforcement of the fillers as domains in the polymeric matrix. The sample of polycarboxylate cement was prepared in P/L ratio of 1.5:1and examined under a scanning electron microscope (JEOL 840) with a magnification of 2500 times.

6/8/2002   10   2500   PAA COMP |—— 9 μm ——|

a

6/8/2002   10   PAA COMP |—— 9 μm ——|
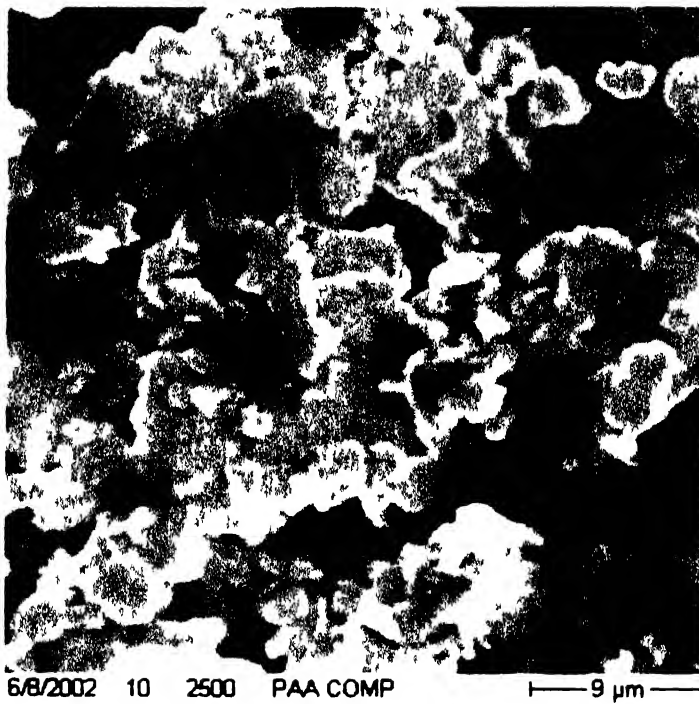
b

FIGURE 4.26 : **SEM** PHOTOGRAPHS OF POLYCARBOXYLATE CEMENT

It is ample clear from the micrographs designated as figure 4.26 (a) and (b) that the ZnO particles are distributed in the form of white globules in the dark background of the polymer matrix. A uniform distribution of ZnO particles throughout the polymer matrix was observed.

4.3: EVALUATION OF POLYCARBOXYLATE CEMENT

The Polycarboxylate cement was evaluated for various properties. For this purpose the Polycarboxylate cement compositions were prepared by mixing the 40% aqueous solution of polyacrylic acid with deactivated Zinc oxide in a P/L ratio 1.5:1. The various properties such as setting time, compressive strength and diametral tensile strength were also evaluated for these samples.

4.31: SETTING TIME

Setting time is the parameter that indicates the ultimate process of setting of any cement. It is an important property in the restorative dentistry. The setting time that is indicated in the literature is 4 to 9 minutes without the reference to P/L ratio. The setting time for the cement sample prepared with P/L ratio 1.5:1 was found to be 4.5 minutes.

4.32: COMPRESSIVE STRENGTH AND DIAMETRAL TENSILE STRENGTH

The compressive strength and diametral tensile strength were measured by, as the process outlined under section 3.21 and 3.22 respectively.

The maximum load values at which the specimen fractured may to some extent depend on the crosshead speed of the device and hence different compressive as well as tensile strengths may result. The universal testing machine was operated at a crosshead speed of 0.05 cm/ min.

Compressive strength:

The maximum load along the long axis at which the specimen fractured was found to be 121.2 kg.

Diameter of the specimen = 6.16 mm

Height of the specimen = 11.9 mm

Compressive strength = 406.51 Kg/ cm^2

Tensile Strength:

The maximum load along the short axis (diametral compression) at which the specimen fractured was found to be 54.3 Kg.

Diameter of the specimen = 6.1 mm

Height of the specimen = 11.85 mm

Tensile strength = 47.8 Kg/ cm^2

SAFETY MEASURES:

While working in the project various measures should be taken for the reason of health and safety. The most important measures were taken when Acrylic acid was polymerized to polyacrylic acid. All those required are described below.

Acrylic acid is moderately toxic when it is ingested or absorbed through the skin. When swallowed, they may cause severe intestinal burns and damage to the gastric tract. The liquids are strongly corrosive to the skin, and especially to the eyes and may destroy tissue upon relatively short contact. Vapours of Acrylic acid are highly irritating to the eyes skin and mucous membranes.

Protection required for safe handling of acrylic acid includes:

- The use of impermeable and splash proof goggles.

- Good ventilation of the work place.

- Upon contact with the monomer, the skin should promptly be washed with sufficient amount of water followed by wash with soap and water.

- Medical consultation is required if any trouble appears.

CONCLUSION

The cement is a replacement for the traditional Zinc phosphate and Zinc oxide eugenol cements. As it is a polymer based dental cement, is less rigid and more liable to creep. Its disadvantage is that it requires greater care in preparation related to the temperature control, initiator percentage and rate of addition of acrylic acid while preparing Polyacrylic acid. Also the powder/liquid ratio is a factor for the performance of the polycarboxylate cement.

As from the IR study, stoichiometric Zinc Polycarboxylate cement is identical to the Zinc polyacrylate salt. Most of the carboxylate groups are present as a neutralized carboxylate salt, however a few free COOH groups remain. A small amount of chelate is also formed along with the Zinc-polyacrylate salt. From the X-Ray diffraction analysis the polycarboxylate cement is found to be predominately amorphous, though a little crystallinity is observed in the cement.

FURTHER SCOPES OF WORK:

Pcarboxylate cements can be prepared by varying the powder/liquid ratio to achieve better performance i.e. to nullify the presence of unreacted COOH groups. The formation of a small amount of chelate and its role in the setting of the cement has to be studied by variation of polyacrylic acid concentration as well as powder/liquid ratio.

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